

**CHARACTERIZATION OF FILLED EPOXY
THIN FILM COMPOSITES FOR DIELECTRIC
APPLICATION**

POH CHEN LING

UNIVERSITI SAINS MALAYSIA

2015

**CHARACTERIZATION OF FILLED EPOXY THIN FILM COMPOSITES
FOR DIELECTRIC APPLICATION**

by

POH CHEN LING

**Thesis submitted in the fulfillment of the requirements
for the degree of
Master of Science**

MAY 2015

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitles “Characterization of Filled Epoxy Thin Film Composites for Dielectric Application”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of Student : Poh Chen Ling

Signature:

Date:

Witness by

Supervisor: Prof Ir. Mariatti Jaafar @ Mustapha

Signature:

Date:

ACKNOWLEDGEMENTS

First of all, I would like to express my deepest gratitude to my supervisor, Professor Dr. Ir. Mariatti Jaafar @ Mustapha for her valuable guidance, caring, motivation and providing me support during my master research. I am sincerely thankful to her for spending valuable times to go through my thesis and provide useful suggestions and corrections. Besides that, I would like to thanks to my co-supervisor, Professor Ahmad Fauzi B. Mohd Noor for providing me advices, encouragement and support during my study. Special thanks goes to Dean of School of Materials and Mineral Resources Engineering (SMMRE), Professor Dr. Hanafi Ismail for helping me towards my postgraduate affairs.

I highly acknowledge the financial support from CREST grant which covers the tuition fees, monthly allowances and supporting this works. I would also thanks to technical staff of SMMRE for their technical advices and assistance. I would like to convey my special thanks to Mr Chuah Tin Poay and Susan Chow See Chin from Intel Microelectronics (M) Sdn Bhd, Penang for their assistance and advices. I would like to thanks to my coursemates for their helps and support during my MSc. Study.

Last but not least, my deepest gratitude goes to my beloved parents and brother for their endless love and financially support. I would like to express my deepest thanks to my beloved friends and boyfriend for their love and care.

TABLE OF CONTENTS

DECLARATION	ii
ACKNOWLEDGEMENT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	ix
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xviii
LIST OF SYMBOLS	xx
LIST OF APPENDICES	xxii
ABSTRAK	xxiii
ABSTRACT	xxiv

CHAPTER 1 INTRODUCTION

1.1 Introduction	1
1.2 Problem Statements	3
1.3 Research Objectives	5
1.4 Scope of Study	5
1.5 Organization of Thesis	6

CHAPTER 2 LITERATURE REVIEW

2.1 Capacitor	8
2.1.1 Types of Capacitor	9
2.1.2 Embedded Capacitor Application	11
2.1.3 Fabrication of Embedded Capacitor	12
2.1.3.1 Spin Coating Process	13

2.2	Polymer Composites	15
2.3	Epoxy	17
2.4	Filler	18
2.4.1	Calcium Carbonate (CaCO_3)	19
2.4.2	Barium titanate (BaTiO_3)	20
2.4.3	Carbon Nanotube (CNT)	22
2.5	Ultrasonication	23
2.6	Filler Functionalization	25
2.6.1	Chemical Functionalization	25
2.6.2	Physical Functionalization	27
2.7	Properties of Dielectric Materials	28
2.7.1	Dielectric Properties	28
2.7.2	Thermal Properties	30
2.7.3	Mechanical Properties	32
2.8	Previous Works on Embedded Capacitor Application	33

CHAPTER 3 MATERIALS AND METHODS

3.1	Materials	36
3.1.1	Epoxy Resin and Curing Agent	36
3.1.2	Filler Materials	38
3.1.3	Materials for Filler Functionalization	39
3.2	Experiment Methods	40
3.2.1	Preparation of Different Types of Fillers Filled Epoxy Thin Film Composites	40

3.2.2	Preparation of Functionalization on MWCNT Filled Epoxy Thin Film Composites	44
3.2.3	Preparation of Untreated and Treated MWCNT Filled OP 392 Epoxy Thin Film Composites	45
3.3	Characterizations	47
3.3.1	Image Analysis	47
3.3.2	Particle Analysis	48
3.3.3	Tensile Properties	48
3.3.4	Dynamic Mechanical Analysis	48
3.3.5	Thermogravimetric Analysis	49
3.3.6	Thermo Mechanical Analysis	49
3.3.7	Dielectric properties	50
3.3.8	Fourier Transform Infrared analysis	51
3.3.9	Raman Spectra Analysis	51
 CHAPTER 4 RESULTS AND DISCUSSION		
4.1	Introduction	52
4.2	Characterization on Morphology of Fillers	52
4.3	Comparison Properties between Mineral CaCO_3 and Precipitated CaCO_3	55
4.3.1	Dielectric Properties	56
4.3.2	Tensile Properties	62
4.3.3	Dynamic Mechanical Properties	66
4.3.4	Thermal Properties	69
4.4	Effect of Different Types of Nanofillers and Filler Loadings	73

4.4.1	Dielectric Properties	73
4.4.2	Tensile Properties	81
4.4.3	Dynamic Mechanical Properties	86
4.4.4	Thermal Properties	89
4.5	Functionalization of MWCNT	92
4.5.1	Fourier Transform Infrared Spectroscopy	92
4.5.2	Raman Spectra	94
4.5.3	Characterization on Morphology of Treated and Untreated MWCNT	96
4.5.4	Dielectric Properties	99
4.5.5	Tensile Properties	102
4.5.6	Dynamic Mechanical Properties	107
4.5.7	Thermal Properties	109
4.6	Comparison Properties between Two Types of Epoxy Resin	113
4.6.1	Dielectric Properties	113
4.6.2	Tensile Properties	116
4.6.3	Dynamic Mechanical Properties	120
4.6.4	Thermal Properties	122
4.6.5	Comparison Properties between Commercial Dielectric Material with Present Study	126

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	128
5.2	Recommendations	129

REFERENCES	131
APPENDICES	143
LIST OF PUBLICATION	146

LIST OF TABLES

	PAGE
Table 3.1: The general properties of DER 332 epoxy and D23 hardener (Materials Safety Data Sheet)	37
Table 3.2: The general properties of OP 392 Part A and Part B (Materials Safety Data Sheet)	38
Table 3.3: Speed and time interval of spin coating process for epoxy thin film composites.	42
Table 4.1: T_5 and T_{onset} of neat epoxy, 15 vol% mineral $CaCO_3$ and 1.5 vol% precipitated $CaCO_3$ filled epoxy thin film composites.	70
Table 4.2: T_g , CTE before T_g and after T_g of neat epoxy, 15 vol% mineral $CaCO_3$ and 1.5 vol% precipitated $CaCO_3$ filled epoxy thin film composites.	73
Table 4.3: T_5 and T_{onset} of of neat epoxy, 1.5 vol% precipitated $CaCO_3$, $BaTiO_3$, and MWCNT filled epoxy thin film composites.	90
Table 4.4: T_g , CTE before T_g and after T_g of neat epoxy, 1.5 vol% precipitated $CaCO_3$, $BaTiO_3$, and MWCNT filled epoxy thin film composites.	91
Table 4.5: I_D/I_G of MWCNT, Triton X-100 treated MWCNT, SDS treated MWCNT and Triton X-100 with AMPTES treated MWCNT.	96

Table 4.6:	T_5 and T_{onset} of neat epoxy, 1.5 vol% treated and untreated MWCNT filled epoxy thin film composites.	111
Table 4.7:	T_g , CTE before T_g and after T_g of neat epoxy, 1.5 vol% treated and untreated filled epoxy thin film composites.	112
Table 4.8:	T_5 and T_{onset} of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	124
Table 4.9:	CTE before T_g and after T_g of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	125
Table 4.10:	Comparison properties between commercial dielectric material (3M Embedded capacitance material) with present study.	127
Table A:	Amount of mineral CaCO_3 and epoxy matrix to produce mineral CaCO_3 filled epoxy thin film composites at various loading.	143
Table B:	Amount of different types of nanofillers and epoxy matrix to produce epoxy thin film composites at various loading.	143
Table C:	Amount of Triton X-100, SDS for treated MWCNT.	144
Table D:	Amount of AMPTES for treated MWCNT.	145

LIST OF FIGURES

	PAGE
Figure 2.1: The set up of capacitor in the presence of an applied electric field (Bennett, 2011).	9
Figure 2.2: Different type of discrete capacitors (a) ceramic (b) mica (c) tantalum (d), (e) polypropylene (f) polystyrene (g) ceramic chip (h-l) electrolytic capacitor (Linsley, 2013).	10
Figure 2.3: Embedded capacitor application (Alam <i>et al.</i> , 2011).	11
Figure 2.4: Lay up of embedded capacitor with PCB (Renaule & Munier, 2012).	12
Figure 2.5: Formation of embedded capacitor film by using common roll coated (Cho <i>et al.</i> , 2004).	13
Figure 2.6: Spin coating process of polymer solution to produce thin film layer (Michler, 2008).	14
Figure 2.7: Schematic reaction between amine hardener with epoxy resin (Hoa, 2009).	18
Figure 2.8: Perovskite structure of Barium Titanate (Wang, 2002).	21
Figure 2.9: Schematic of the reaction between silane group with CNT wall (Santos <i>et al.</i> , 2011).	26
Figure 3.1: Chemical formula of (a) Triton X-100 (b) SDS (c) AMPTES.	39

Figure 3.2:	Flow chart on preparation of epoxy thin film composites.	43
Figure 3.3:	Flow chart on preparation of OP 392 epoxy thin film composites.	46
Figure 3.4:	Preparation specimen for dielectric test.	50
Figure 4.1:	Particle morphology of (a) mineral CaCO_3 (b) precipitated CaCO_3 (c) BaTiO_3 and (d) MWCNT (magnification at 1000x for (a) by SEM and magnification at 44,000x for (b), (c) and (d) by TEM).	53
Figure 4.2:	Distribution particle size of (a) mineral CaCO_3 (b) precipitated CaCO_3 and BaTiO_3 .	54
Figure 4.3:	Specific capacitance of (a) mineral CaCO_3 and (b) precipitated CaCO_3 filled epoxy thin film composites at various frequencies.	57
Figure 4.4:	Dielectric constant of (a) mineral CaCO_3 and (b) precipitated CaCO_3 filled epoxy thin film composites at various frequencies.	59
Figure 4.5:	Dielectric loss of various filler loading of (a) mineral CaCO_3 and (b) precipitated CaCO_3 filled epoxy thin film composites.	61
Figure 4.6:	Tensile strength of mineral CaCO_3 and precipitated CaCO_3 filled epoxy thin film composites.	63

Figure 4.7:	Young's modulus of mineral CaCO_3 and precipitated CaCO_3 filled epoxy thin film composites.	64
Figure 4.8:	SEM micrograph of fracture surface of (a) and (b) neat epoxy (c) and (d) 15 vol% of mineral CaCO_3 (e) and (f) 1.5 vol% of precipitated CaCO_3 filled epoxy thin film composites (Magnification of 1000x for (a),(c) and (e) 5000x for (b) and (d), 10,000x for (f)).	65
Figure 4.9:	(a) Storage modulus (b) loss modulus (c) loss factor $\tan \delta$ of neat epoxy, 15 vol% mineral CaCO_3 and 1.5 vol% precipitated CaCO_3 filled epoxy thin film composites.	67
Figure 4.10:	(a) TGA (b) DTG of neat epoxy, 15 vol% mineral CaCO_3 and 1.5 vol% precipitated CaCO_3 filled epoxy thin film composites.	70
Figure 4.11:	(a) Specific capacitance (b) Dielectric constant of BaTiO_3 filled epoxy thin film composite at various frequencies.	74
Figure 4.12:	(a) Specific capacitance (b) Dielectric constant of MWCNT filled epoxy thin film composite at various frequencies.	75
Figure 4.13:	(a) Specific capacitance (b) Dielectric constant of 2 vol% of precipitated CaCO_3 , BaTiO_3 and MWCNT filled epoxy thin film composite at various frequencies.	77
Figure 4.14:	Dielectric loss of BaTiO_3 filled epoxy thin film composite at various frequencies.	78

Figure 4.15:	Dielectric loss of MWCNT filled epoxy thin film composite at various frequencies.	79
Figure 4.16:	Dielectric loss of precipitated CaCO_3 and BaTiO_3 filled epoxy thin film composite at 1 kHz.	80
Figure 4.17:	(a) Tensile strength (b) Young's modulus of precipitated CaCO_3 , BaTiO_3 and MWCNT filled epoxy thin film composites.	81
Figure 4.18:	SEM micrograph of fracture surface of (a) and (b) neat epoxy (c) and (d) 1.5 vol% of precipitated CaCO_3 (e) and (f) 1.5 vol% of BaTiO_3 (g) and (h) 1.5 vol% of MWCNT filled epoxy thin film composites (Magnification of 1000x for (a),(c),(e) and (g) 5,000x for (b), 10,000x for (d) and (f) and 20,000x for (h)).	84
Figure 4.19:	(a) Storage modulus (b) loss modulus (c) loss factor $\tan \delta$ of neat epoxy, 1.5 vol% precipitated CaCO_3 , BaTiO_3 and MWCNT filled epoxy thin film composites.	87
Figure 4.20:	(a) TGA (b) DTG of neat epoxy, 1.5 vol% precipitated CaCO_3 , BaTiO_3 , and MWCNT filled epoxy thin film composites.	89
Figure 4.21:	FTIR spectra of neat epoxy, MWCNT, Triton X-100 treated MWCNT, SDS treated MWCNT and Triton X-100 with AMPTES treated MWCNT filled epoxy thin film composites.	94

Figure 4.22:	Raman spectra of MWCNT, Triton X-100 treated MWCNT, SDS treated MWCNT and Triton X-100 with AMPTES treated MWCNT.	95
Figure 4.23:	TEM images of (a) and (b) untreated MWCNT, (c) and (d) Triton X-100 treated MWCNT, (e) and (f) SDS treated MWCNT, (g) and (h) Triton X-100 with AMPTES treated MWCNT (magnification of 38000x for (a), (c), (e) and (g) and 450000x for (b), (d), (f), (h)).	97
Figure 4.24:	(a) Specific capacitance (b) Dielectric constant of 1.5 vol% of treated and untreated MWCNT filled epoxy thin film composite at various frequencies.	100
Figure 4.25:	Dielectric loss of 1.5 vol% of treated and untreated MWCNT filled epoxy thin film composite at 1 kHz.	101
Figure 4.26:	(a) Tensile strength (b) Young's modulus of treated and untreated MWCNT filled epoxy thin film composites.	103
Figure 4.27:	SEM micrographs of fracture surface of (a) and (b) 1.5 vol% of MWCNT/epoxy composite, (c) and (d) 1.5 vol% of Triton X-100 treated MWCNT/epoxy composite, (e) and (f) 1.5 vol% of SDS treated MWCNT/epoxy composites, (g) and (h) 1.5 vol% of Triton X-100 with AMPTES treated MWCNT/epoxy composite (magnification: 1000× for (a),(c),(e) and (g); 20,000× for (b),(d),(f) and (h)).	105

Figure 4.28:	(a) Storage modulus (b) loss modulus (c) loss factor $\tan \delta$ of neat epoxy, 1.5 vol% treated and untreated MWCNT filled epoxy thin film composites.	108
Figure 4.29:	(a) TGA and (b) DTG curve of 1.5 vol% treated and untreated MWCNT filled epoxy thin film composites.	110
Figure 4.30:	(a) Specific capacitance (b) dielectric constant of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	114
Figure 4.31:	Dielectric loss of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	115
Figure 4.32:	(a) Tensile strength (b) Young's modulus of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	117
Figure 4.33:	SEM micrographs of fracture surface of (a) and (b) 1.5 vol% of MWCNT/OP 392 epoxy composites, (c) and (d) 1.5 vol% of Triton X-100 treated MWCNT/OP 392 epoxy composites (e) and (f) 1.5 vol% of SDS treated MWCNT/OP 392 epoxy composite (magnification: 1000 \times for (a),(c) and (e); 20,000 \times for (b),(d) and (h)).	118
Figure 4.34:	(a) Storage modulus (b) loss modulus and (c) $\tan \delta$ of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.	121

Figure 4.35: (a) TGA (b) DTG of 1.5 vol% treated and untreated MWCNT filled OP 392 and DER 332 epoxy thin film composites.

123

LIST OF ABBREVIATIONS

PCB	Printed Circuit Board
CMC	Critical Micelle Concentration
CaCO ₃	Calcium Carbonate
BaTiO ₃	Barium Titanate
CNT	Carbon Nanotube
SWCNT	Single-walled Carbon Nanotube
MWCNT	Multi-walled Carbon Nanotube
BSTZ	Barium Strontium Titanate Zirconium
Ag	Silver
Al	Aluminium
DGEBA	Bisphenol-A Diglycidylether
PMMA	Polymethyl Methacrylate
PTFE	Polytetrafluoroethylene
Triton X-100	Polyoxyethylene Octyl Phenyl Ether
SDS	Sodium Dodecyl Sulfate
CTAB	Cetyltrimethylammonium Bromide
AMPTES	3-(Aminopropyl)triethoxysilane
GPTMS	3-Glycidoxypropyltrimethoxy Silane
H ₂ O ₂	Hydrogen Peroxide
CO ₂	Carbon Dioxide
DI	Deionized Water
TEM	Transmission Electron Microscope
HRTEM	High Resolution Transmission Electron Microscope
SEM	Scanning Electron Microscope

DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric
TMA	Thermomechanical Analysis
CTE	Coefficient of Thermal Expansion

LIST OF SYMBOLS

Q	Charge
V	Voltage
C	Capacitance
ϵ	Permittivity of the Material
ϵ_0	Permittivity of the Vacuum
k	Dielectric Constant
A	Area
d	Separation between Two Conductors
t	Thickness of the Specimens
V_f	Volume Fraction of Filler
V_m	Matrix Volume Fraction
W_f	Weight of Filler
W_m	Weight of Matrix
$W_{\text{surfactant}}$	weight of surfactant
W_{AMPTES}	weight of AMPTES
ρ_f	Density of Filler
ρ_m	Density of Matrix
E_f	Filler Modulus
E_m	Matrix Modulus
E'	Storage Modulus
E''	Loss Modulus
I_D	Intensity Ratio of D Band
I_G	Intensity Ratio of G Band
T_g	Glass Transition Temperature

T_5	5 % Weight Loss Temperature
T_{onset}	Onset Degradation Temperature

LIST OF APPENDICES

	PAGE
APPENDIX A: Amount of fillers and matrix for epoxy thin film composites at different filler loading	143
APPENDIX B: Calculation for the amount of surfactant and MWCNT in treated system	144
APPENDIX C: Calculation for the amount of AMPTES and MWCNT in treated system	145

PENCIRIAN KOMPOSIT FILEM NIPIS EPOKSI TERISI UNTUK KEGUNAAN DIELEKTRIK

ABSTRAK

Dalam kajian ini, sifat dielektrik, mekanikal dan terma komposit filem nipis epoksi terisi pelbagai jenis pengisi telah dikaji. Bahan pengisi dan epoksi disediakan dengan menggunakan pencampuran ultrasonik dan komposit filem nipis difabrikasi dengan kaedah lapisan putaran. Dalam peringkat pertama, komposit filem nipis epoksi terisi mineral kalsium karbonat (mineral CaCO_3) dan kalsium karbonat termendak (CaCO_3 termendak) telah dikaji. Adalah didapati bahawa CaCO_3 termendak mempamerkan sifat dielektrik dan kekuatan tensil yang lebih baik manakala mineral CaCO_3 mempamerkan sifat terma dan moduli yang lebih baik. Dalam peringkat kedua, sifat bagi pelbagai jenis pengisi (CaCO_3 termendak, barium titanat (BaTiO_3) and tiubnano karbon berbilang dinding (MWCNT)) telah dikaji. Adalah didapati bahawa BaTiO_3 dan MWCNT mempamerkan sifat dielektrik dan kemuatan yang lebih baik dibandingkan dengan CaCO_3 termendak. Memandangkan sifat dielektrik dan kemuatan adalah penting untuk kegunaan kapasitor, MWCNT dipilih untuk kajian kefungsiannya dalam peringkat ketiga. Rawatan MWCNT oleh pelbagai jenis kefungsiannya menggunakan polioksietilena oktil fenil eter (Triton X-100), natrium dodesil sulfat (SDS), and 3-(aminopropil)triethoxysilane (AMPTES)) digunakan untuk merawat MWCNT. Adalah didapati bahawa rawatan MWCNT mempunyai sifat dielektrik dan mekanikal lebih baik daripada MWCNT tanpa rawatan. Sifat dielektrik yang lebih kurang sama diperhatikan dalam perbandingan bagi dua jenis epoksi (OP 392 epoksi dan DER 332 epoksi) dengan 1.5 vol% MWCNT tanpa rawatan dan MWCNT dengan rawatan oleh Triton X-100 dan SDS. Komposit filem nipis OP 392 epoksi mempamerkan suhu peralihan kaca (T_g) yang tinggi dan kekuatan tensil yang lebih rendah dibandingkan dengan komposit filem nipis DER 332 epoksi. Secara keseluruhannya, komposit filem nipis epoksi terisi MWCNT dengan rawatan oleh Triton X-100 adalah bahan yang paling sesuai untuk kegunaan dielektrik.